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PREPARATION AND CHARACTERIZATION OF CU<sub>2</sub>ZN<sub>1</sub>-X<sub>1</sub>MGES<sub>4</sub>(U)  
BROWN UNIV PROVIDENCE RI DEPT OF CHEMISTRY  
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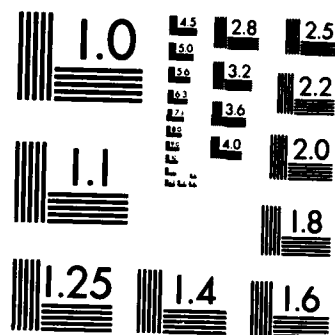
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PREPARATION AND CHARACTERIZATION OF  $\text{Cu}_2\text{Zn}_{1-x}\text{Mn}_x\text{GeS}_4$

by

E. Honig, H-S. Shen, G-Q. Qao, K. Doverspike

R. Kershaw, K. Dwight and A. Wold

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# PREPARATION AND CHARACTERIZATION OF $\text{Cu}_2\text{Zn}_{1-x}\text{Mn}_x\text{GeS}_4$

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## ABSTRACT

Single crystals of  $\text{Cu}_2\text{Zn}_{1-x}\text{Mn}_x\text{GeS}_4$  ( $x = 0, 0.03, 0.05, 0.10, 1.0$ ) have been grown by chemical vapor transport. These crystallize with the wurtz-stannite structure. Magnetic measurements show that the Curie-Weiss law is obeyed. Manganese exhibits the expected spin only moment and the Weiss constants become more negative as the manganese concentration increases. Ambient temperature resistivities decrease with increasing manganese concentration. Two band transitions are observed for all materials in the range 1.9-2.1 eV.

MATERIALS INDEX: Vapor transport growth; Magnetic properties.

## Introduction

Many compounds crystallizing with a diamond-like structure are well known and have been extensively studied (1). These have been predominantly the II-VI and III-V semiconductors (e.g. ZnS and GaAs) as well as ternary compounds crystallizing with the chalcopyrite structure (e.g.  $\text{ZnGeP}_2$ ) (2). A large class of structurally related compounds are the quaternary chalcogenides  $\text{Cu}_2\text{B(II)C(IV)X}_4$  where B = Mn, Fe, Co, Ni, Zn, Cd, Hg; C = Si, Ge, Sn; and X = S, Se (3-7). Most of these compounds crystallize with superstructures of zinc blende or wurtzite by an ordering of the cation sites. This yields the orthorhombic wurtz-stannite (space group  $\text{Pmn}2_1$ ) or the tetragonal stannite (space group  $\text{I}\bar{4}2\text{m}$ ) structures depicted in Fig. 1. In these structures, alternating layers of mixed B(II) and C(IV) cations are separated by layers of Cu atoms. Both cationic and anionic sites are tetrahedrally coordinated with each anion surrounded by two copper, one B(II) and one C(IV) atom. These materials have been grown by chemical vapor transport and solid state reaction (3-7). There have been a few reports regarding some of their electrical, magnetic, optical and mechanical properties (7-9). However, none of these investigated the properties of single crystal solid solutions or, indeed, if these could at all be grown. This study reports the preparation and characterization of single crystals of  $\text{Cu}_2\text{Zn}_{1-x}\text{Mn}_x\text{GeS}_4$  ( $x = 0, 0.03, 0.05, 0.10, 1.0$ ).

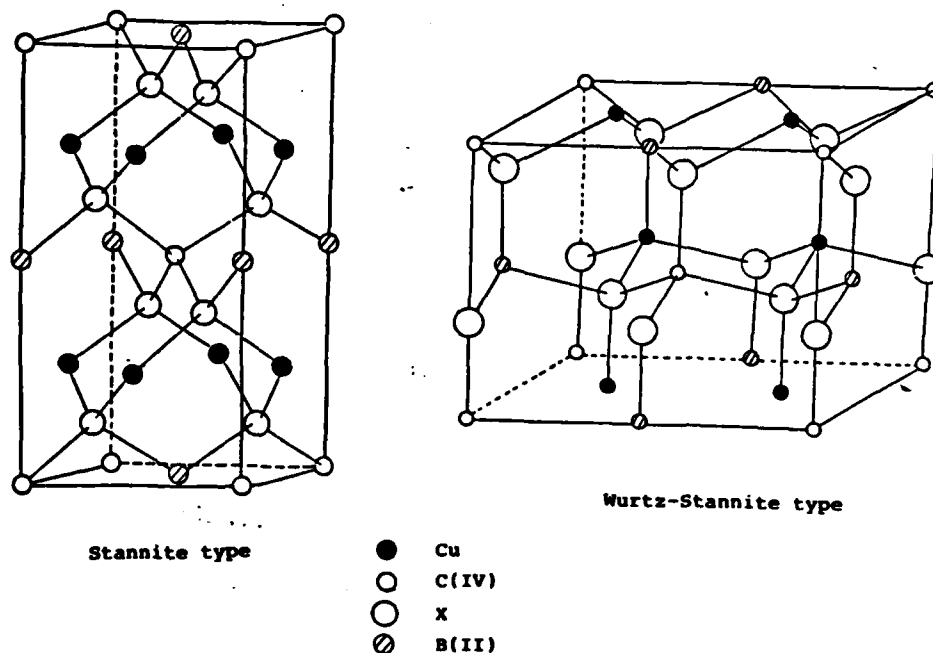


Fig. 1. Stannite and Wurtz-Stannite Structures.

### Experimental

#### Single Crystal Growth

Single crystals of  $\text{Cu}_2\text{Zn}_{1-x}\text{Mn}_x\text{GeS}_4$  ( $x = 0, 0.03, 0.05, 0.10, 1.0$ ) were grown by chemical vapor transport using iodine as the transport agent. Copper (Matthey 99.999%) and zinc (Gallard and Schlesinger, 99.999%) were reduced in an 85%Ar/15% $\text{H}_2$  atmosphere prior to use. Manganese (Gallard and Schlesinger, 99.99%) was deoxidized by heating for 24 hours at 800°C in a silica tube which contain titanium metal in a separate compartment. Sulfur (Gallard and Schlesinger 99.999%) was sublimed prior to use while germanium (Cominco, 7-9's 40  $\Omega$ -cm) was used as received.

Stoichiometric weights of the elements were introduced into a silica tube, which was then evacuated to  $5 \times 10^{-5}$  torr, and five mg/cc of iodine were added. The tube was sealed off and enclosed in a tightly wound Kanthal coil (to even

out temperature gradients) and the whole assembly was placed in a three-zone furnace. The crystal growth temperature program consisted of setting the furnace to back transport mode for 2 days (growth zone hotter than charge zone), equilibrating the furnace to the maximum reaction temperature for 2 days and, finally, cooling the central zone at 2°C/hr to the growth temperature. Optimum growth conditions were obtained when the maximum reaction temperature of the charge was 900°C for  $x = 0, 0.03, 0.05, 0.10$ , and 800°C for  $x = 1.0$ . A temperature gradient of  $\Delta T = 50^\circ\text{C}$  between the charge and the growth zones was used for crystal growth in all cases. The transport process was run for ten days.

#### X-ray analysis

Powder diffraction patterns of ground single crystals were obtained with a Philips diffractometer using monochromatic radiation from a high intensity copper source ( $\lambda\text{-CuK}\alpha_1 = 1.5405\text{\AA}$ ). For qualitative phase identification, patterns were taken with a scan rate of  $1^\circ 2\theta/\text{min}$ , while cell parameters were determined from scans taken at  $0.25^\circ 2\theta/\text{min}$ . Diffraction patterns were obtained over the range  $12^\circ < 2\theta < 72^\circ$  and the reflections were indexed on unit cells previously determined for  $x = 0, 1.0$ . Precise lattice parameters were obtained from these reflections using a least-squares refinement program which corrects for the systematic errors of the diffractometer.

#### Magnetic, Optical and Electrical Measurements

Magnetic measurements were performed using the Faraday balance previously described (10). Magnetic susceptibilities were obtained as a function of temperature from 77 to 300 K at a field strength of 10.4 kOe and the field dependence from 6.22 to 10.4 kOe was also determined at these temperature extremes. The data was corrected for core diamagnetism using the value obtained for  $x = 0$ .

Measurements of absorption coefficients were made with an Oriel Model 1724 monochromator, an Oriel G 772-5400 long pass filter and a calibrated silicon diode detector. Absorption values were calculated from the responses with and without the crystal in the beam.

The van der Pauw method was used to measure electrical resistivities (11). Contacts were made by ultrasonic soldering of indium directly onto samples and ohmic behavior was established by measuring the current-voltage characteristics. The sign of the majority carriers was determined from the qualitative measurement of the Seebeck effect.

#### Results and Discussion

Single crystals in the series  $\text{Cu}_2\text{Zn}_{1-x}\text{Mn}_x\text{GeS}_4$  ( $x = 0, 0.03, 0.05, 0.10, 1.0$ ) have been grown by chemical vapor transport using iodine as the transport agent. Polyhedral crystals ( $2 \times 2 \times 1 \text{ mm}^3$ ) were obtained for  $x = 1.0$  while the samples with lower manganese concentration ( $x = 0, 0.03, 0.05, 0.10$ ) yielded blade-like crystals ( $7 \times 5 \times 1 \text{ mm}^3$ ). All crystals were orange in color, although for  $x = 1.0$  the crystals were more opaque. All samples crystallize with the wurtz-stannite structure, which has an orthorhombic unit cell. Table 1 summarizes the x-ray data.

Magnetic susceptibility measurements were obtained on samples with  $x = 0, 0.03, 0.05, 0.10$  and  $1.0$  and were used as a probe for the concentration of manganese in the crystals. All samples exhibited paramagnetic behavior and could be fit to the Curie-Weiss law  $\chi = C/(T-\theta)$  where  $C$  and  $\theta$  are the Curie and Weiss constants, respectively. The susceptibilities for all samples were found to be independent of field ( $6.22 - 10.4$  kOe) at  $77\text{K}$  and ambient temperature, indicating the absence of any ferromagnetic impurity.

Table 1

CELL CONSTANTS\* FOR  $\text{Cu}_2\text{Zn}_{1-x}\text{Mn}_x\text{GeS}_4$

x	a(Å)	b(Å)	c(Å)	ref.
0	7.509(1)	6.471(1)	6.186(1)	this work
	7.504	6.474	6.185	3
0.03	7.508(2)	6.473(1)	6.183(1)	this work
0.05	7.512(1)	6.476(2)	6.188(1)	this work
0.10	7.510(2)	6.481(2)	6.190(1)	this work
1.0	7.610(1)	6.513(1)	6.236(1)	this work
	7.608	6.511	6.236	3

\*Based on an orthorhombic unit cell, space group  $\text{Pmn}2_1$ .

Paramagnetic susceptibilities of crystals with nominal composition  $x \leq 0.1$  were found to be reproducible not only within each run but also between runs. This shows that consistent manganese concentrations could be obtained via the transport process. All values of  $\chi$  were corrected for the core diamagnetism of  $\text{Cu}_2\text{ZnGeS}_4$  which was found to be  $3.32 \times 10^{-7}$  emu/g. [Values of  $3.37$  and  $3.27 \times 10^{-7}$  emu/g were obtained at ambient and liquid nitrogen temperatures]. Magnetic data are summarized in Table 2. The ratio of  $C_x/C_{\text{Mn}+2}$  gives a measure of the manganese substitution in the structure. From Table 2 it is apparent that the crystals grow with the same stoichiometry as the charge. The negative Weiss constants obtained for all samples indicate that the net interactions of the magnetic moments are antiferromagnetic in nature. They also become less negative as the manganese concentration decreases. This is consistent with a decrease in the concentration of nearest-neighbor magnetic ions.

Crystals with  $x = 1$  evidenced slight variations in their paramagnetic susceptibility. The results shown in Fig. 2 were obtained from two crystals from the same run. One gives a Weiss constant  $\theta$  of  $-15\text{K}$ , the other  $-10\text{K}$ . The resistivity data for these same two crystals are shown in Fig. 3. The difference between their two curves is small and may not be related to the difference in their Weiss constants. The small differences observed in the magnetic and electrical properties are consistent with small deviations from ideal stoichiometry.

Qualitative Seebeck measurements indicated that the crystals were p-type. Crystals with  $x \leq 0.1$  had resistivities greater than  $10^3 \Omega\text{-cm}$ .



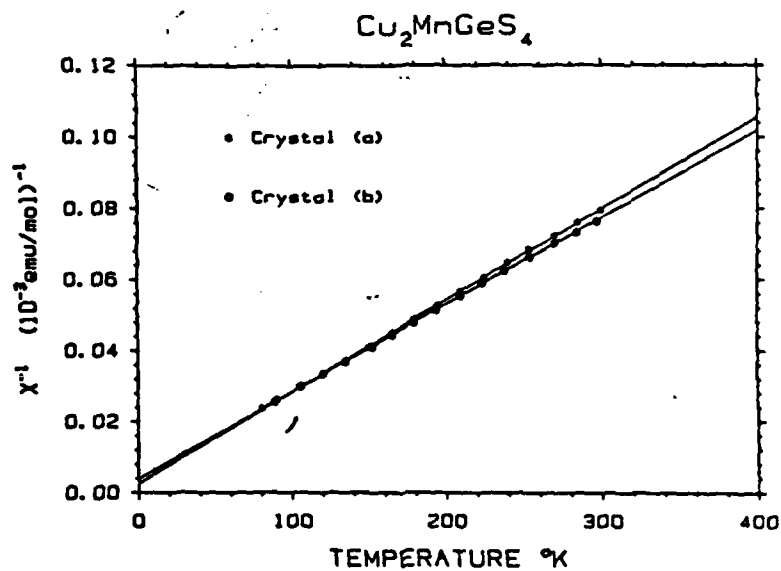


Fig. 2.  $\chi^{-1}$  as a function of temperature for two crystals of  $\text{Cu}_2\text{MnGeS}_4$  for a single run.

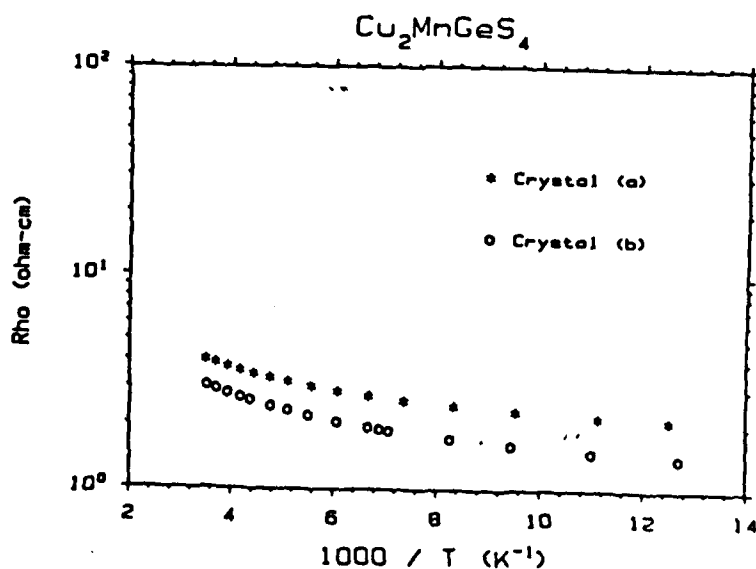


Fig. 3. Resistivity as a function of temperature for the two crystals of  $\text{Cu}_2\text{MnGeS}_4$  reported in Fig. 2.

The indirect optical band gaps were obtained from plots of  $(\alpha h \nu)^{1/2}$  vs energy. Although other stannite and wurtz-stannite quaternaries containing B(II) = Mn, Fe, Co, Ni have been reported, there appears to be no data pertaining to their optical character. These materials have been reported to be black (2). However, in the present study polished samples of  $\text{Cu}_2\text{MnGeS}_4$  ( $t = 0.3\text{mm}$ ) resulted in an orange color under transmitted light similar to that for crystals with lower manganese concentration ( $x < 1.0$ ).

The optical band gap was found to be  $2.0 \pm 0.05$  eV for all low values of  $x$ , and  $1.90 \pm 0.05$  eV for  $x = 1.0$ . In addition, for all these samples, the graph of  $(\alpha h \nu)^{1/2}$  vs energy showed a sudden increase in slope at  $2.1 \pm 0.1$  eV. This "kink" indicates the existence of a second band transition (12).

Table 2

MAGNETIC DATA FOR  $\text{Cu}_2\text{Zn}_{1-x}\text{Mn}_x\text{GeS}_4$

Nominal Composition	$C_x$	$\frac{a}{C_x/C_{\text{Mn}}^{2+}}$	$\theta(\text{K})$
0.03	0.1298	0.030	-5.0
0.05	0.2232	0.051	-5.3
0.10	0.4348	0.099	-7.0
1.00	4.1(2)	0.93(4)	-13(3)

(a)  $C_{\text{Mn}}^{2+}$  is the Curie constant calculated for free  $\text{Mn}^{2+}$  from  $C = N\mu^2/3k$ .

Table 3

ELECTRICAL DATA FOR  $\text{Cu}_2\text{Zn}_{1-x}\text{Mn}_x\text{GeS}_4$

$x$	$\rho (\Omega\text{-cm})$
1	5(2)
0.1	$4 \times 10^3$
0	$1.6 \times 10^4$

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